NOTE ON THE CHANDRASEKHAR MODEL OF THE OPTICAL ACTIVITY OF CRYSTALS

Jan Říha, Kamila Sváčková, Ivo Vyšín

Department of Theoretical Physics, Natural Science Faculty of Palacký University, Svobody 26, **771 46 Olomouc**, Czech Republic

ABSTRACT: In this paper we discuss more wide applicability of the Chandrasekhar model of coupled oscillators in the optical rotatory dispersion of the crystals. We solve the problem using the Chandrasekhar model of two coupled oscillators in the case when we include all couplings between adjacent oscillators on the helix that is given by the crystal structure. Further we discuss the results of coupled oscillators models in the case of the including of the couplings between even and odd oscillators on the helix. The ORD results obtained after the approximations of the oscillator strengths verify that these couplings have the important influence on the crystal ORD.

1 Introduction

The phenomenon of the optical activity (OA) has two aspects which arise from the interaction of the radiation with matter - dispersive and absorptive. These aspects are the optical rotatory dispersion (ORD) and the circular dichroism (CD). It is well known that ORD is the dependency of the rotation of the linear polarized light per unit length on the frequency ω or on the wave length λ. The CD is the ellipticity per unit length of the wave getting off the crystals. In the difference from the ORD, which is nonzeroth in a wide frequency region, the CD is nonzeroth only in a very narrow frequency region in the absorption region.

The important group of optically active crystals are the crystals with screw axis of symmetry belonging to the space groups of symmetry D_3^4 and D_3^6. The typical representatives of these crystals are α-quartz, cinnabar, tellurium, selen, camphor, benzil. The optical activity of these crystals due to asymmetrical originating of the crystal structure because the molecules or atoms forming the

crystals are not optically active. Camphor is the exception because his molecules are optically active so that his optical activity has two sides - molecular and crystalline.

In the past the OA of crystals was studied by more authors and their works are based on the different theories. We can introduce the theory of excitons [1, 2, 3, 4], the theory of coupled oscillators [5, 6, 7] or Lagrangian formalism [8]. But it is known that the theory of coupled oscillators gives the results which are very good applicable in the fitting of the experimental data of OA. The model of coupled oscillators was for the first time used by Chandrasekhar [5] which has applicated the Kuhn model [9] of two coupled oscillators which represent the smallest unit of the optical active crystal. He has used the following model: The first oscillator lies in the plane $z = 0$ and its position is given by direction cosines α, β, γ. The second oscillator lies in the plane $z = d$ and its direction of vibration is turned by the angle θ around the z axis which is parallel to the crystal axis c. Both oscillators lie on the helix which is given by the crystal structure. The z axis (crystal axis o) has the direction of the propagation of the linear polarized electromagnetic wave. Both coupled oscillators forming one compound oscillator are identical. We denote the coupling constant between oscillators as Q_1. Chandrasekhar further has assumed that the number of compound oscillators in the volume unit is $N/2$, where N is the number of single oscillators in the volume unit. The influence of the interactions between oscillators belonging to the other helices is neglected because of another type of couplings.

Becouse of the interaction between single oscillators in the compound oscillator the natural frequency ω_0 is split into two frequencies ω_1 and ω_2 of normal modes of vibrations. For these normal modes Chandrasekhar has solved the dispersion theory of refractive indices for the propagation of the left and the right circularly polarized wave into which the linear polarized wave is split in the optically active medium. It is well known that the medium containing coupled oscillators is optically active and therefore it must be characterized by the different refractive indices n_l and n_r for the left and the right circularly polarized wave. Chandrasekhar has solved the dispersion theory semiclasically, he has introduced into results the oscillator strengths but he has assumed that the oscillator strengths of the normal modes of vibrations are the same.

Chandrasekhar has solved his model of optical activity for the α-quartz. Because the CD is not measured for the α-quartz and therefore nor the ORD in the absorption region Chandrasekhar has assumed the oscillators as undamped.

Later V. Vyšín [7] has removed Chandrasekhar's simplifications in the approach of the oscillator strengths of the normal modes of vibrations and he has obtained for the ORD which is denoted by $\rho(\omega)$ the formula

$$\rho(\omega) = \frac{\pi N d e^2 \omega^2}{mc^2} \left(\alpha^2 + \beta^2\right) \sin\theta \left[\frac{-f_{g_1}}{\omega_1^2 - \omega^2} + \frac{f_{q_2}}{\omega_2^2 - \omega^2}\right], \quad (1)$$

where f_{q_1} and f_{q_2} are the oscillator strengths of the normal modes of vibrations,

m is the mass of the single oscillator, e his electric charge and c is the velocity of the light. The frequencies of the normal modes are $\omega_1^2 = \omega_0^2 + Q_1$, $\omega_2^2 = \omega_0^2 - Q_1$. Because the splitting of the frequencies of the normal modes is very small we can (1) rewrite in the form containing the natural frequency of single oscillators

$$\rho(\omega) = \frac{\pi N d e^2 \omega^2}{mc^2} \left(\alpha^2 + \beta^2\right) \sin\theta \cdot \left[\frac{f_{q_2} - f_{g_1}}{\omega_0^2 - \omega^2} + \frac{Q_1\left(f_{q_1} + f_{q_2}\right)}{\left(\omega_0^2 - \omega^2\right)^2}\right]. \qquad (2)$$

We see that the ORD based on the two coupled oscillator model leads in general to the two member formula. The first term on the right side of eq. (2) is known as Drude's term and the second term is known as Chandrasekhar's term. This is problem because we don't know the oscillator strengths for the real crystals. We can solve the oscillator strengths only in approximations. For example in the approximation of the linear harmonic oscillator $f_{q_1} = f_{q_2} = f_0$ (the Chandrasekhar approximation) the formula (2) leads only to the Chandrasekhar formula

$$\rho(\omega) = \frac{2\pi N d e^2 Q_1 f_0}{mc^2} \left(\alpha^2 + \beta^2\right) \sin\theta \cdot \frac{\omega^2}{\left(\omega_0^2 - \omega^2\right)^2}. \qquad (3)$$

On the other hand we can solve the oscillator strengths in the Heitler - London approximation [10] which gives the result

$$\frac{f_{q_1}}{\omega_1} = \frac{f_{q_2}}{\omega_2} = \frac{f_0}{\omega_0} \qquad (4)$$

and then ORD is given by the formula

$$\rho(\omega) = \frac{\pi N e^2 d Q_1 f_0}{mc^2} \left(\alpha^2 + \beta^2\right) \sin\theta \cdot \frac{\omega^2 \left(\omega_0^2 + \omega^2\right)}{\omega_0^2 \left(\omega_0^2 - \omega^2\right)^2}. \qquad (5)$$

We note that the formula (5) is the Agranovich type [1, 2] which was derived by the exciton's theory.

The formula (2) or its special forms (3) and (5) was used in many works to describe the experimental data of ORD of the crystals, for example of the tellur [11, 12, 13], of the α-quartz [14, 15] or of the crystal $Bi_{12}GeO_{20}$ [16, 17] and without exception with good results. On the other hand we think that the Chandrasekhar model still contains some simplifications which we want to solve in this paper.

The Chandrasekhar model assumes that $N/2$ coupled oscillators, where N is the number of single oscillators, exist in the volume unit. But it means that we have $N/2$ isolated compound oscillators in the volume unit. This idea desribes for example the system of randomly oriented isolated non-interacting molecules. But in the crystals all adjacent molecules or atoms interact on the helices. It means that the second oscillator in the any compound oscillator is at the same time the first oscillator in the next compound oscillator. It is the first question

how the results of the Chandrasekhar model will change in the case when we include all couplings between all adjacent oscillators into this model.

The second question follows from the fact that the two coupled oscillators model neglect all other couplings between oscillators on one helix. It is possible in the case when all oscillators lie on the line because the value of the coupling constant decreases with third power of the distance. But it is not true in the real crystals where the diameter and the step of the helix are comparable. In these cases we must include also the couplings between even and odd oscillators on the helices. Further in the crystals with the space groups of symmetry D_3^4 and D_3^6 the vibration directions of the adjacent oscillators contain the angle $\theta = 120deg$. The vibration directions of the even or odd oscillators contain the angle $\theta = 240deg$. From the formulae (2), (3) or (5) we see that the sense of ORD depends on the value of $\sin\theta$. It means that the couplings between even and odd oscillators on the helices have the opposite effect on the ORD in compare with the couplings between adjacent oscillators. We note that in the crystals with space groups of symmetry D_3^4 and D_3^6 the couplings between the first and the fourth oscillators which are randomly oriented don't have the influence on the OA and then the other couplings are really neglectable.

2 The influence of the couplings between all adjacent oscillators

We can discuss this problem by means of the results of our previous paper [18]. In this paper we have solved the application of the ORD Chandrasekhar model of three coupled oscillators. We have added to the Chandrasekhar model of two coupled oscillators the third oscillator which lies on the helix in the plane $z = -d$ and its vibration direction is turned by the angle $-\theta$ around z axis with respect to the oscillator in the plane $z = 0$. We include also as Chandrasekhar only the couplings between adjacent oscillators. The number of these compound oscillators in the volume unit is $N/3$.

The solving method is also the same as Chandrasekhar's with the exception that the natural frequency ω_0 of each oscillators is split into three frequencies ω_1, ω_2 and ω_3 and also the ORD result contains three terms regards to (1) that is

$$
\begin{aligned}
\rho(\omega) \;=\; & \frac{2\pi N d e^2 \omega^2}{3mc^2} \left(\alpha^2 + \beta^2 \right) \sin\theta \\
& \times \left[\frac{-\left(\sqrt{2} + 2\cos\theta\right) f_{q_1}}{\omega_1^2 - \omega^2} + \frac{4 f_{q_2} \cos\theta}{\omega_2^2 - \omega^2} + \frac{\left(\sqrt{2} - 2\cos\theta\right) f_{q_3}}{\omega_3^2 - \omega^2} \right], \quad (6)
\end{aligned}
$$

where $\omega_1^2 = \omega_0^2 + \sqrt{2}Q_1$, $\omega_2^2 = \omega_0^2$ and $\omega_3^2 = \omega_0^2 - \sqrt{2}Q_1$. We can rewrite this result with the natural frequency of oscillators ω_0 but this result is involved too. We express this result only in the approximations of the oscillators strengths. In the

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Chandrasekhar linear harmonic oscillator approximation $f_{q_1} = f_{q_2} = f_{q_3} = f_0$ we get

$$\rho(\omega) = \frac{8\pi N d e^2 Q_1 f_0 \omega^2}{3mc^2} \left(\alpha^2 + \beta^2\right) \sin\theta \cdot \left[\frac{1}{(\omega_0^2 - \omega^2)^2} - \frac{2Q_1 \cos\theta}{(\omega_0^2 - \omega^2)^3}\right]. \quad (7)$$

We see that the second term in the square brackets is very small with respect to the first one. It contains the coupling constant Q_1 that is very small and the denominator of this term is in the frequency region far from absorption much greater than the denominator of the first term. From this reason the second term can be neglected.

In the Heitler - London approximation that is given by the extended relation (4) we have

$$\rho(\omega) = \frac{4\pi N d e^2 Q_1 f_0 \left(\alpha^2 + \beta^2\right) \sin\theta}{3mc^2} \cdot \left[\frac{\omega^2 \left(\omega_0^2 + \omega^2\right)}{\omega_0^2 \left(\omega_0^2 - \omega^2\right)^2} - \frac{2Q_1 \cos\theta}{(\omega_0^2 - \omega^2)^3}\right] \quad (8)$$

and we can neglect again the second term in the square brackets. But then the results of two and three coupled oscillators are very similar, they differ only in the multiplicative constant 4/3. We see the sense of this constant if we compare the results for one compound oscillator. We must divide the results of two coupled oscillators model (3) and (5) by $N/2$ (the number of compound oscillators in the volume unit) and the results of the three coupled oscillators model (7) and (8) by $N/3$. By the comparing of corresponding results we see that one triad of the coupled oscillators has the twofold effect on the ORD than one couple. From this it follows that the effects of couplings between adjacent oscillators are aditive. If we want to include all couplings in the two coupled oscillators model we must take as the number of coupled oscillators N (in the case $N \to \infty$) because the number of couplings is the same as the number of single oscillators. In the case of three coupled oscillators model we take N/2 as the number of compound oscillators in the volume unit etc. Then both models of two and three coupled oscillators give the same results in the case of the including of the couplings between adjacent oscillators only. The mistake of this conclusion is given by the neglecting of the second terms in the square brackets in (7) and (8) but we can assume that in the cases of small couplings in the crystals the mistake is neglectable.

From our conclusions in this section it follows that if we use our results in the approximation of experimental data of ORD of the crystals we get different values of unknown parameters in these formulae. For example the ORD of α-quartz was approximated by Chandrasekhar's and Vyšín's results of the two coupled oscillators model. The unknown parameters were the oscillator strengths of the normal modes of vibrations. The values of the oscillator strengths were in the results that are assumed as true smaller as the number of valence shell electrons [19]. In the other results the values of the oscillator strengths were greater. But after our correction of the results of the two coupled oscillators model we get for

all oscillator strengths a half of values and it would be difficult to say what results of the approximations of the experimental data are true and what the values of all oscillator strengths will be too small. It is the next reason for the assertion that we must include also the couplings between even and odd oscillators which due to its opposite effect on the ORD return for example in the case of α-quartz the results of the approximations of oscillator strengths to the values that they have in [19].

3 The influence of the couplings between even and odd oscillators

The smallest system in which we can include the coupling between even or odd oscillators in the helix is the system of three coupled oscillators if we include also the coupling between the first and the third oscillator. The scheme of this system is the same as in the previous section. We characterize the coupling between the first and the third oscillator by the coupling constant Q_2. Regarding to the previous section we use now the value $N/2$ as the number of compound oscillators where N is the number of single oscillators in the volume unit. It means that the last single oscillator in any compound oscillator is the first single oscillator in the next compound oscillator on the helix.

The solving ORD of this system by the Chandrasekhar semiclassical model is described in [20]. We get for the ORD the three member formula

$$
\begin{aligned}
\rho(\omega) \;=\; & \frac{4\pi N de^2\omega^2}{mc^2}\left(\alpha^2+\beta^2\right)\sin\theta \\
& \times\left[\frac{\frac{-(2\cos\theta+A_1)}{2+A_1^2}f_{q_1}}{\omega_1^2-\omega^2}+\frac{f_{q_2}\cos\theta}{\omega_2^2-\omega^2}+\frac{\frac{-(2\cos\theta+A_3)}{2+A_3^2}f_{q_3}}{\omega_3^2-\omega^2}\right],
\end{aligned}
\tag{9}
$$

where $\omega_1^2=\omega_0^2+\frac{Q_2+\sqrt{8Q_1^2+Q_2^2}}{2}$, $\omega_2^2=\omega_0^2-Q_2$ and $\omega_3^2=\omega_0^2+\frac{Q_2-\sqrt{8Q_1^2+Q_2^2}}{2}$ and A_1, A_3 are $A_1=\frac{-Q_2+\sqrt{8Q_1^2+Q_2^2}}{2Q_1}$, $A_3=\frac{-Q_2-\sqrt{8Q_1^2+Q_2^2}}{2Q_1}$. We see that by the expression of this result regarding to the natural frequency we obtain complicated result and its form is also described in [20]. Let us again be interested in the form of the result after the approximations of the oscillator strengths. If we neglect as in previous section all the terms containing $1/(\omega_0^2-\omega^2)^3$ we get in the Chandrasekhar approximation the result

$$
\rho(\omega)=\frac{4\pi N de^2 f_0\left(\alpha^2+\beta^2\right)\sin\theta\cdot(Q_1+2Q_2\cos\theta)}{mc^2}\cdot\frac{\omega^2}{\left(\omega_0^2-\omega^2\right)^2}
\tag{10}
$$

and in the Heitler - London approximation

$$
\rho(\omega)=\frac{2\pi N de^2 f_0\left(\alpha^2+\beta^2\right)\sin\theta\cdot(Q_1+2Q_2\cos\theta)}{mc^2}\cdot\frac{\omega^2\left(\omega_0^2+\omega^2\right)}{\omega_0^2\left(\omega_0^2-\omega^2\right)^2}.
\tag{11}
$$

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If we compare these results with the results (7) and (8) after their discussion, it means after neglecting the terms with $1/(\omega_0^2 - \omega^2)^3$ and after their correction by including all couplings between adjacent oscillators (the coefficient $N/3$ is substituted by $N/2$), we see that the results (10) and (11) are different only in the coefficient $Q_1 + 2Q_2 \cos\theta$ which substitutes the coupling constant Q_1 in the eqs. (7) and (8). In the crystals belonging to the space groups of symmetry D_3^4 and D_3^6 is $\cos\theta = -0.5$ and the coefficient gives the value $Q_1 - Q_2$. The couplings between even and odd oscillators have indeed the opposite efect on the ORD. Besides we include in our three coupled oscillators model all couplings between adjacent oscillators on the helices but only a half of couplings between even and odd oscillators. Nevertheless the influence of couplings with couplings constants Q_1 and Q_2 has the same form. If we include all couplings between even and odd oscillators the influence of these couplings will be, of course, much greater but we don't know the expression for this influence.

Even and odd coupled oscillators on the helices are not contacted and we cannot use the method of the contacted compound oscillators from the section 2. If we want to solve this problem exactly we should solve the model of $\bar{N}$ coupled oscillators where $\bar{N}$ is the number of all single oscillators on one helix and in this model we should include all couplings between adjacent, even and odd oscillators. This model is not, of course, really solvable.

From this reason we have proceeded by another way. We have solved further the models of four, five etc. coupled oscillators in which we have included the couplings between adjacent, even and odd oscillators and the results we have expressed only with the natural frequency ω_0 and only in the approximations of the oscillator strengths of the normal modes of vibrations and only for the crystals with the space groups of symmetry D_3^4 and D_3^6. Based on these results we have found the tendency in the expression that contains the coupling coefficient Q_2 and we have looked the limit of this expression with increased number of oscillators in the models. We show now the solving of the four coupled oscillators model. The solving of other models is similar but more complicated and we discuss only the results.

3.1 The four coupled oscillator model of the optical rotatory dispersion of crystals

We extend the three coupled oscillators model by the fourth oscillator which lies on the helix in the plane $z = 2d$ and his vibration direction is turned by the angle 2θ around z axis with respect to the vibration direction of the oscillator in the plane $z = 0$. The coupling constant Q_1 describes the coupling between adjacent oscillators and the constant Q_2 describes the couplings between the first and the third and between the second and the fourth oscillators. The motion

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equations of the oscillators in the fields of the left and the right circularly polarized wave are

$$\ddot{r}_1 + \omega_0^2 r_1 + Q_1 r_2 + Q_2 r_3 = F_1^{l,r},$$
$$\ddot{r}_2 + \omega_0^2 r_2 + Q_1 r_1 + Q_1 r_3 + Q_2 r_4 = F_2^{l,r},$$
$$\ddot{r}_3 + \omega_0^2 r_3 + Q_2 r_1 + Q_1 r_2 + Q_1 r_4 = F_3^{l,r}, \qquad (12)$$
$$\ddot{r}_4 + \omega_0^2 r_4 + Q_2 r_2 + Q_1 r_3 = F_4^{l,r},$$

where r_1, r_2, r_3, r_4 are the displacements of oscillators from equilibrium, F denotes the projection of functioning forces to the motion direction of oscillators divided by the masses m of oscillators (electrons). In all terms in equation (12) and further in the sign $\pm$ hold the $+$ sign for the left and the $-$ sign for the right cicularly polarized wave. The electric field vector $\vec{E}$ has in our case the components

$$E_x^{l,r} = E_0 \cos(\omega t - k_{l,r} z),$$
$$E_y^{l,r} = \pm E_0 \sin(\omega t - k_{l,r} z) \qquad (13)$$

and then we can express the forces $F_\eta^{l,r}(\eta = 1, 2, 3, 4)$ as

$$F_1^{l,r} = \frac{eE_0}{m}[(\alpha \cos\theta + \beta \sin\theta)\cos(\omega t + \phi_{l,r})$$
$$\pm(-\alpha \sin\theta + \beta \cos\theta)\sin(\omega t + \phi_{l,r})],$$
$$F_2^{l,r} = \frac{eE_0}{m}(\alpha \cos\omega t \pm \beta \sin\omega t),$$
$$F_3^{l,r} = \frac{eE_0}{m}[(\alpha \cos\theta - \beta \sin\theta)\cos(\omega t - \phi_{l,r}) \qquad (14)$$
$$\pm(\alpha \sin\theta + \beta \cos\theta)\sin(\omega t - \phi_{l,r})],$$
$$F_4^{l,r} = \frac{eE_0}{m}[(\alpha \cos 2\theta - \beta \sin 2\theta)\cos(\omega t - 2\phi_{l,r})$$
$$\pm(\alpha \sin 2\theta + \beta \cos 2\theta)\sin(\omega t - 2\phi_{l,r})],$$

where e is the electron charge and $\phi_{l,r} = k_{l,r} = \frac{2\pi n_{l,r} d}{\lambda} = \frac{n_{l,r}\omega d}{c}$ is a phase shift.
We may express relations (12) in the normal coordinates which are

$$q_1 = \frac{1}{\sqrt{2(1+A_1^2)}}(r_1 + A_1 r_2 + A_1 r_3 + r_4),$$
$$q_2 = \frac{1}{\sqrt{2(1+A_2^2)}}(r_1 + A_2 r_2 + A_2 r_3 + r_4),$$
$$q_3 = \frac{1}{\sqrt{2(1+A_3^2)}}(r_1 + A_3 r_2 - A_3 r_3 - r_4), \qquad (15)$$
$$q_4 = \frac{1}{\sqrt{2(1+A_4^2)}}(r_1 + A_4 r_2 - A_4 r_3 - r_4),$$

where

$$A_1 = \frac{Q_1 + \sqrt{5Q_1^2 + 8Q_1 Q_2 + 4Q_2^2}}{2(Q_1 + Q_2)},$$
$$A_2 = \frac{Q_1 - \sqrt{5Q_1^2 + 8Q_1 Q_2 + 4Q_2^2}}{2(Q_1 + Q_2)},$$
$$A_3 = \frac{Q_1 - \sqrt{5Q_1^2 - 8Q_1 Q_2 + 4Q_2^2}}{2(-Q_1 + Q_2)}, \qquad (16)$$
$$A_4 = \frac{Q_1 + \sqrt{5Q_1^2 - 8Q_1 Q_2 + 4Q_2^2}}{2(-Q_1 + Q_2)}.$$

As a result of coupling the natural frequency ω_0 of each oscillator splits into four characteristic frequencies of the normal modes of vibrations

$$
\begin{aligned}
\omega_1^2 &= \omega_0^2 + \frac{Q_1 + \sqrt{5Q_1^2 + 8Q_1 Q_2 + 4Q_2^2}}{2}, \\
\omega_2^2 &= \omega_0^2 + \frac{Q_1 - \sqrt{5Q_1^2 + 8Q_1 Q_2 + 4Q_2^2}}{2}, \\
\omega_3^2 &= \omega_0^2 - \frac{Q_1 - \sqrt{5Q_1^2 - 8Q_1 Q_2 + 4Q_2^2}}{2}, \\
\omega_4^2 &= \omega_0^2 - \frac{Q_1 + \sqrt{5Q_1^2 - 8Q_1 Q_2 + 4Q_2^2}}{2}.
\end{aligned}
\tag{17}
$$

Now it is possible to rewrite the motion equations of each oscillator

$$
\ddot{q}_\eta^{l,r} + \omega_\eta^2 q_\eta^{l,r} = R_{q_\eta}^{l,r}, \qquad \eta = 1,2,3,4,
\tag{18}
$$

where $R_{q_\eta}^{l,r}$ are the forces in the normal coordinates. For them we get in general expression

$$
R_{q_\eta}^{l,r} = \frac{eE_0}{m}(a_{q_\eta}^{l,r})\cos(\omega t + \sigma_{q_\eta}^{l,r}), \qquad \eta = 1,2,3,4
\tag{19}
$$

where $\sigma_{q_\eta}^{l,r}$ is a phase shift and for $(a_{q_\eta}^{l,r})$ we have derived

$$
\begin{aligned}
(a_{q1}^{l,r})^2 &= \tfrac{\alpha^2+\beta^2}{1+A_1^2}[1 \pm 3\phi_{l,r}\sin\theta - 3\cos\theta + 4\cos^3\theta \mp 12\phi_{l,r}\cos^2\theta \sin\theta \\
&\quad -2A_1(1 - \cos\theta - 2\cos^2\theta \pm \phi_{l,r}\sin\theta \pm 4\phi_{l,r}\sin\theta\cos\theta) \\
&\qquad +A_1^2(1 + \cos\theta \mp \phi_{l,r}\sin\theta)] \\
(a_{q2}^{l,r})^2 &= \tfrac{\alpha^2+\beta^2}{1+A_2^2}[1 \pm 3\phi_{l,r}\sin\theta - 3\cos\theta + 4\cos^3\theta \mp 12\phi_{l,r}\cos^2\theta \sin\theta \\
&\quad -2A_2(1 - \cos\theta - 2\cos^2\theta \pm \phi_{l,r}\sin\theta \pm 4\phi_{l,r}\sin\theta\cos\theta) \\
&\qquad +A_2^2(1 + \cos\theta \mp \phi_{l,r}\sin\theta)] \\
(a_{q3}^{l,r})^2 &= \tfrac{\alpha^2+\beta^2}{1+A_3^2}[1 \mp 3\phi_{l,r}\sin\theta + 3\cos\theta - 4\cos^3\theta \pm 12\phi_{l,r}\cos^2\theta \sin\theta \\
&\quad +2A_3(1 + \cos\theta - 2\cos^2\theta \mp \phi_{l,r}\sin\theta \pm 4\phi_{l,r}\sin\theta\cos\theta) \\
&\qquad +A_3^2(1 - \cos\theta \pm \phi_{l,r}\sin\theta)] \\
(a_{q4}^{l,r})^2 &= \tfrac{\alpha^2+\beta^2}{1+A_4^2}[1 \mp 3\phi_{l,r}\sin\theta + 3\cos\theta - 4\cos^3\theta \pm 12\phi_{l,r}\cos^2\theta \sin\theta \\
&\quad +2A_4(1 + \cos\theta - 2\cos^2\theta \mp \phi_{l,r}\sin\theta \pm 4\phi_{l,r}\sin\theta\cos\theta) \\
&\qquad +A_4^2(1 - \cos\theta \pm \phi_{l,r}\sin\theta)].
\end{aligned}
\tag{20}
$$

Let's substitute eq. (19) into eq. (18), we get

$$
\ddot{q}_\eta^{l,r} + \omega_\eta^2 q_\eta^{l,r} = (a_{q_\eta}^{l,r})\frac{eE_0}{m}\cos(\omega t + \sigma_{q_\eta}^{l,r})
\tag{21}
$$

and the solution of these equations is

$$
q_\eta = (a_{q_\eta}^{l,r})\frac{eE_0}{m}\cdot\frac{\cos(\omega t + \sigma_{q_\eta}^{l,r})}{\omega_\eta^2 - \omega^2}.
\tag{22}
$$

The propagating light wave induces the dipole moments $d_{q_\eta}^{l,r}$ which are

$$
d_{q_\eta}^{l,r} = q_\eta(a_{q_\eta}^{l,r})f_{q_\eta}e
\tag{23}
$$

or using (22)

$$d_{q_\eta}^{l,r} = (a_{q_\eta}^{l,r})^2 \frac{f_{q_\eta} e^2 E_0}{m} \cdot \frac{\cos(\omega t + \sigma_{q_\eta}^{l,r})}{\omega_\eta^2 - \omega^2}, \tag{24}$$

where f_{q_η} are the oscillator strengths in the normal modes of vibrations. The mean polarizability per volume unit is

$$\chi_{q_\eta}^{l,r} = \frac{N' d_{q_\eta}^{l,r}}{E_0 \cos(\omega t + \sigma_{q_\eta}^{l,r})} = \frac{N d_{q_\eta}^{l,r}}{3 E_0 \cos(\omega t + \sigma_{q_\eta}^{l,r})}, \tag{25}$$

where N' is the number of compound oscilators in the volume unit. We see that in our case $N' = N/3$ where N is the number of isolated oscillators.

For the refractive indices of the crystals we have the Drude-Sellmaier dispersion relation

$$n_{l,r}^2 - 1 = 4\pi \sum_{\eta=1}^{4} \chi_{q_\eta}^{l,r} = \frac{4\pi N e^2}{3m} \sum_{\eta=1}^{4} (a_{q_\eta}^{l,r})^2 \frac{f_{q_\eta}}{\omega_\eta^2 - \omega^2}. \tag{26}$$

From eq. (26) we are able to solve the relation

$$n_l^2 - n_r^2 = \frac{4\pi N e^2}{3m} \sum_{\eta=1}^{4} \frac{[(a_{q_\eta}^l)^2 - (a_{q_\eta}^r)^2] f_{q_\eta}}{\omega_\eta^2 - \omega^2} \tag{27}$$

and using (20) we can calculate for the expression in square brackets

$$\begin{aligned}
(a_{q_1}^l)^2 - (a_{q_1}^r)^2 &= \frac{(\alpha^2+\beta^2)(\phi_l+\phi_r)}{1+A_1^2} \sin\theta (3 - 12\cos^2\theta \\
&\quad -2A_1 - 8A_1\cos\theta - A_1^2), \\
(a_{q_2}^l)^2 - (a_{q_2}^r)^2 &= \frac{(\alpha^2+\beta^2)(\phi_l+\phi_r)}{1+A_2^2} \sin\theta (3 - 12\cos^2\theta \\
&\quad -2A_2 - 8A_2\cos\theta - A_2^2), \\
(a_{q_3}^l)^2 - (a_{q_3}^r)^2 &= \frac{(\alpha^2+\beta^2)(\phi_l+\phi_r)}{1+A_3^2} \sin\theta (-3 + 12\cos^2\theta \\
&\quad -2A_3 + 8A_3\cos\theta + A_3^2), \\
(a_{q_4}^l)^2 - (a_{q_4}^r)^2 &= \frac{(\alpha^2+\beta^2)(\phi_l+\phi_r)}{1+A_4^2} \sin\theta (-3 + 12\cos^2\theta \\
&\quad -2A_4 + 8A_4\cos\theta + A_4^2).
\end{aligned} \tag{28}$$

In eq. (28) we can write $(\phi_l + \phi_r) = \frac{\omega d(n_l+n_r)}{c}$ and $n_l^2 - n_r^2 = (n_l - n_r)(n_l + n_r)$. Using the well known formula for the ORD $\rho(\omega) = \frac{\omega}{2c}(n_l - n_r)$ we obtain

$$\begin{aligned}
\rho(\omega) &= \frac{2\pi N d e^2}{3c^2} \omega^2(\alpha^2 + \beta^2)\sin\theta \\
&\quad \times \left[\frac{(3 - 12\cos^2\theta - 2A_1 - 8A_1\cos\theta - A_1^2)f_{q_1}}{(1+A_1^2)(\omega_1^2 - \omega^2)} \right. \\
&\quad \left. + \frac{(3 - 12\cos^2\theta - 2A_2 - 8A_2\cos\theta - A_2^2)f_{q_2}}{(1+A_2^2)(\omega_2^2 - \omega^2)} \right.
\end{aligned}$$

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$$+\frac{(-3 + 12\cos^2\theta - 2A_3 + 8A_3\cos\theta + A_3^2)f_{q3}}{(1 + A_3^2)(\omega_3^2 - \omega^2)}$$

$$+\frac{(-3 + 12\cos^2\theta - 2A_4 + 8A_3\cos\theta + A_4^2)f_{q4}}{(1 + A_4^2)(\omega_4^2 - \omega^2)}\Bigg]. \tag{29}$$

Using eqs. (17) we can rewrite the formula (29) to the form which contains the natural frequency of the oscillators only but we see that we would get the complicated expression. We will discuss the result (29) only in the approximations of the oscillator strengths and also only for the crystals with the space groups of symmmmetry D_3^4 and D_3^6 for which $\theta = 120$ deg and therefore $\cos\theta = -1/2$.

3.2 Discussion

We will express as in the sections 1, 2 and 3 the result (29) in the linear harmonic oscillator approximation and in the Heitler - London approximation of the oscillator strengths. In all results we neglect all the small terms containing the expressions $1/(\omega_0^2 - \omega^2)$ of the order higher than second. These terms contain with the exception of the great value of the denominator also the higher orders of the small coupling constants Q_1 and Q_2 in the numerators.

At first we will use in the discussion of the result (29) the Chandrasekhar linear harmonic oscillator approximation where we can calculate with equation $f_{q_1} = f_{q_2} = f_{q_3} = f_{q_4} = f_0$. In this case we obtain the ORD formula of the Chandrasekhar type

$$\rho(\omega) = \frac{4\pi N de^2 f_0 (\alpha^2 + \beta^2)\sin\theta \cdot \left(Q_1 - \frac{4}{3}Q_2\right)}{mc^2} \cdot \frac{\omega^2}{(\omega_0^2 - \omega^2)^2}. \tag{30}$$

The Heitler-London aproximation is in the case of four coupled oscillators given by the relation

$$\frac{f_{q_1}}{\omega_1} = \frac{f_{q_2}}{\omega_2} = \frac{f_{q_3}}{\omega_3} = \frac{f_{q_4}}{\omega_4} = \frac{f_0}{\omega_0} \tag{31}$$

and using eqs. (17) and taking again into account that Q_1 and Q_2 are small quantities we can simplify expressions for the oscillator strengths to the form

$$\begin{aligned}
f_{q_1} &= f_0(1 + \frac{Q_1 + \sqrt{5Q_1^2 + 8Q_1Q_2 + 4Q_2^2}}{4\omega_0^2}), \\
f_{q_2} &= f_0(1 + \frac{Q_1 - \sqrt{5Q_1^2 + 8Q_1Q_2 + 4Q_2^2}}{4\omega_0^2}), \\
f_{q_3} &= f_0(1 - \frac{Q_1 - \sqrt{5Q_1^2 - 8Q_1Q_2 + 4Q_2^2}}{4\omega_0^2}), \\
f_{q_4} &= f_0(1 - \frac{Q_1 + \sqrt{5Q_1^2 - 8Q_1Q_2 + 4Q_2^2}}{4\omega_0^2}).
\end{aligned} \tag{32}$$

Now we substitute these relations into eq. (29) and we obtain

$$\rho(\omega) = \frac{2\pi N de^2 f_0}{3mc^2}\frac{\omega^2}{\omega_0^2}(\alpha^2 + \beta^2)\sin\theta$$

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$$\times \left[-\frac{3Q_1 - 4Q_2}{\omega_0^2 - \omega^2} + \frac{2(3Q_1\omega_0^2 - 4Q_2\omega_0^2 - 2Q_1^2 + 2Q_1Q_2)}{(\omega_0^2 - \omega^2)^2} \right] \quad (33)$$

and after neglecting the terms Q_1^2 and Q_1Q_2 and adding the terms in the square brackets we have the formula of the Agranovich type

$$\rho(\omega) = \frac{2\pi Nde^2 f_0(\alpha^2 + \beta^2)\sin\theta \cdot (Q_1 - \frac{4}{3}Q_2)}{mc^2} \cdot \frac{\omega^2(\omega_0^2 + \omega^2)}{\omega_0^2(\omega_0^2 - \omega^2)^2}. \quad (34)$$

We see that applying the linear harmonic oscillator aproximation and the Heitler-London aproximation to the general ORD formula (29) of four coupled oscillator model we obtained for the crystals belonging to the space groups of symmetry D_3^4 and D_3^6 the Chandrasekhar (30) and the Agranovich (34) formulae again. Both formulae contain the same expression $Q_1 - \frac{4}{3}Q_2$. Let's also note the results of solving three coupled oscillator model published in [20] where these formulae contain the expression $Q_1 - Q_2$.

We obtain the similar results also in the five, six etc. oscillator models. In the linear harmonic oscillator and in the Heitler - London approximation we get again the Chandrasekhar and the Agranovich formulae which are different only in the constant containing the coupling constants Q_1 and Q_2. This constant has for the five oscillator model the form $Q_1 - \frac{3}{2}Q_2$, in the six oscillator model the form $Q_1 - \frac{8}{5}Q_2$ etc.

These results give the possibility to suppose the form of the ORD formulae for general $\bar{N}$ coupled oscillator model. We obtain the Chandrasekhar formula in the form

$$\rho(\omega) = \frac{4\pi Nde^2 f_0(\alpha^2 + \beta^2)\sin\theta \cdot \left(Q_1 - \frac{2(\bar{N}-2)}{\bar{N}-1}Q_2\right)}{mc^2} \cdot \frac{\omega^2}{(\omega_0^2 - \omega^2)^2}, \quad (35)$$

where $\bar{N}-1$ is the number of coupling between neighbouring oscillators and $\bar{N}-2$ the number of coupling between odd and even oscillators in the model. It means that for the practical case $\bar{N} \to \infty$ we have

$$\rho(\omega) = \frac{4\pi Nde^2(\alpha^2 + \beta^2)\sin\theta \cdot (Q_1 - 2Q_2)}{mc^2} \cdot \frac{\omega^2}{(\omega_0^2 - \omega^2)^2}. \quad (36)$$

The same results we can write for the Agranovich formula:

$$\rho(\omega) = \frac{2\pi Nde^2 f_0(\alpha^2 + \beta^2)\sin\theta \cdot (Q_1 - \frac{2(\bar{N}-2)}{\bar{N}-1}Q_2)}{mc^2} \cdot \frac{\omega^2(\omega_0^2 + \omega^2)}{\omega_0^2(\omega_0^2 - \omega^2)^2} \quad (37)$$

and for $\bar{N} \to \infty$

$$\rho(\omega) = \frac{2\pi Nde^2 f_0(\alpha^2 + \beta^2)\sin\theta \cdot (Q_1 - 2Q_2)}{mc^2} \cdot \frac{\omega^2(\omega_0^2 + \omega^2)}{\omega_0^2(\omega_0^2 - \omega^2)^2}. \quad (38)$$

We see that the expression $Q_1 - 2Q_2$ is the common limit of the coefficients containing the coupling constants in the final ORD formulae in the case $\bar{N} \to \infty$.

4 Conclusions

In this paper we have proved that with the Chandrasekhar ORD two coupled oscillator model we can include all couplings between adjacent oscillators on the helix that is given by the crystal structure. We have solved that the influence of the couplings between adjacent oscillators in the cases when the second single oscillator in the first compound oscillator is the first oscillator in the second compound oscillator we can hold as aditive (the mistake in this conclusion is neglectable). For the including of all couplings between adjacent oscillators is sufficient to take in the Chandrasekhar model that the number of single oscillators in the volume unit is the same as the number of the couplings between adjacent oscillators. The same results were proved for the models of three and four coupled oscillators - the parts of the ORD results that contain the coupling constant between adjacent oscillators Q_1 are identical in all models.

From the crystal structure it follows that we cannot neglect the couplings between even and odd oscillators on the helix. We can assume for the real crystal that the value of the coupling constant between even and odd oscillators Q_2 is comparable with the value of the coupling constant between adjacent oscillators Q_1. Further we have proved that in the crystals with the space groups of symmetry D_3^4 and D_3^6 the couplings between even and odd oscillators have the opposite effect on the ORD than the couplings between adjacent oscillators.

The first coupled oscillator model in which we can include the coupling between even or odd oscillators is the three oscillator model. But using the previous conclusion this model can include all couplings between adjacent oscillators and only a half of couplings between even and odd oscillators on the helix. Besides we cannot assume these couplings as aditive because they function between single oscillators inside of the compound oscillators - for example in the three oscillator model the second oscillator in the compound oscillator is in the fact coupled also with the second oscillator in the adjacent compound oscillator (becouse in the used model the last single oscillator in any compound oscillator is the first single oscillator in the adjacent compound oscillator).

From this reason we have further solved the models of four, five etc. coupled oscillators. In these models the number of the included couplings between even and odd oscillators increases and the results can be generalized. By this way we have proved that the couplings between even and odd oscillators also have the aditive effects. The ORD results of the three oscillators model after the approximations of the oscillator strengths of the normal modes of vibrations contain the coefficient $Q_1 - Q_2$ (for the crystals with space groups of symmetry D_3^4 and D_3^6). In the limit of $\bar{N}$ coupled oscillators for $\bar{N} \to \infty$ it was derived the coefficient $Q_1 - 2Q_2$. This also means that the relative influence of the couplings between even and odd oscillators on the ORD is twofold in comparison with the couplings between adjacent oscillators.

We can formally obtain the generalized ORD results of the $\bar{N}$ coupled oscil-

lators model after the approximations of the oscillator strengths using the three oscillators model in which we denote the value of coupling between the first and the third oscillators as $2Q_2$. We can say that this conclusion is practically acceptable only after using the results of the three oscillator model in the numerical approximations of the experimental ORD data for example of α-quartz or tellur.

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